

Interfacial Tension Relationships Between Contiguous Phases

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

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Henry Brown
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INTERFACIAL TENSION OF MERCURY IN CONTACT WITH ORGANIC LIQUIDS

A study of the literature shows comparatively great discrepancies in the recorded values for the interfacial tension of mercury against different liquids, but fails to disclose the cause of these discrepancies. Impurities present in the materials used or difference in methods employed might account for the variations observed. Harkins and Grafton¹ using the drop weight method obtained a value of 375 dynes/cm. for water against mercury, while Burdon and Oliphant² using the sessile drop method obtained a value of 427 dynes/cm. for the same system. It will be noted that the first mentioned method is a dynamic method; the second a static method.

Inasmuch as we were in immediate need of the most accurate interfacial tension data obtainable, it was decided to carry out a series of measurements making use of both a dynamic method and a static method so that their degree of accuracy might be compared. Accordingly, the drop weight method and the capillary rise method were adopted for use. As our work progressed it was found that the values obtained by these two methods showed comparatively good agreement throughout. Some of the values obtained were not, however, in close agreement with generally accepted values in the literature. A brief description of methods and some of the results obtained follow.

(1) Harkins and Grafton, *J. Am. Chem. Soc.*, **42**, 2534 (1920).

(2) Burdon and Oliphant, *Trans. Faraday Soc.*, **23**, 205 (1927).

Apparatus and Experimental Procedure

Drop Weight Method.—A sketch of the drop weight apparatus used is given in Fig. 1. In this apparatus, a modification of that of Harkins,³ the dropping tip was made of Pyrex tubing and was selected after examining for circularity many feet of tubing of

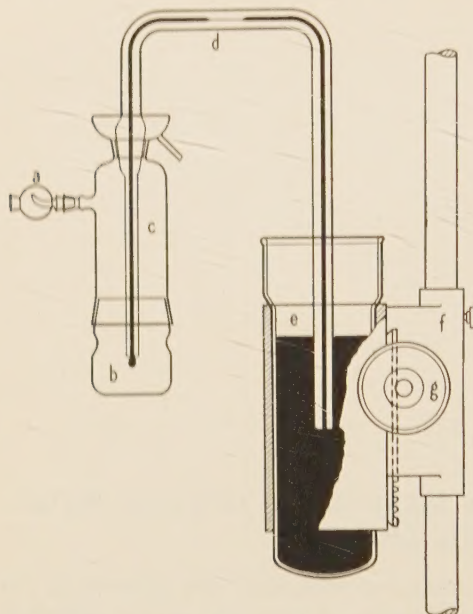


Fig. 1.—Drop weight method for mercury against liquids and saturated vapors.

inner diameter 1.4 to 1.2 mm. (the size used by Harkins and co-workers). In cutting the pieces of tubing a sharp scratch was made with a tungsten edged knife and on pulling the tubing apart at the scratch mark it was found that in many cases the break left a plane surface with an exceedingly sharp edged inner bore normal to the length of the tube. This is the most desirable kind of tip for use with mercury. The diameter of the inner bore of the tip used was 1.242 ± 0.001 mm. (measured with a comparator along eight different diameters).

The dropping tip was sealed to a tube which had a very fine constriction as indicated in the figure. With this fine constriction and with the ratchet and pinion device to alter the head of the mercury in the reservoir, the rate of fall of the drops could be suitably controlled. The tube *d* was held firmly in place on a stable support. This support was separate from the one carrying the reservoir of mercury *e* in order that no vibrations

caused by operating the ratchet and pinion would be communicated to the hanging drop. The jacket *c* was connected to the tubing *d* by means of a ground glass joint (it was found unnecessary to use the mercury seal on this joint). Six cups of type *b* were ground to fit jacket *c*. The apparatus was placed in a large air thermostat ($120 \times 130 \times 80$ cm.) which kept the temperature constant to $\pm 0.05^\circ$.

The determinations were carried out in the following manner. Enough pure liquid was distilled directly into cups *b*, which had been previously cleaned, steamed and dried, so that when the cups were placed in position the liquid covered the dropping tip (about 10 cc. of liquid in each cup). The cups were then covered with ground-glass plates and allowed to stand for about one hour in the thermostat before measurements were started. Usually 7 or 8 drops of mercury were collected in each cup. The drops were allowed to form in the course of about three minutes, and then by lowering the mercury head they were allowed to detach in the course of about two minutes. In placing the cups in position for the measurements it is essential that no air bubbles be trapped against the tip as these may cling to the drop and thus invalidate the correction for buoyancy of the mercury drop.

After the drops had been collected, most of the lighter liquid used was drawn off from the mercury by means of suction applied to a small pipet. This pipet was provided

(3) Harkins and Brown, *J. Am. Chem. Soc.*, **41**, 499 (1919).

with a trap, and was similar in construction to a Drechsel test-tube. The mercury was next covered with acetone and the acetone solution was then drawn off. Finally the cup with the mercury was placed near a fan to evaporate all the acetone. In about fifteen minutes the mercury was ready for weighing.

In none of the measurements were erratic results obtained. This was doubtless due to the razor-edged sharpness of the inner bore of the tip used, as well as to the bulging form of the drop, and to the very high degree of purity of all of the liquids used. It was found that in nearly every case the measurements could be duplicated to within about 0.3%.

Capillary Rise Method.—A diagrammatic sketch of the capillary rise (or capillary depression) apparatus⁴ used is shown in Fig. 2. The entire apparatus was of Pyrex glass. The internal diameters of the cups *M* and *N* were 4 cm. In making a measurement the following procedure was observed.

Mercury was drawn from a reservoir and allowed to flow through capillary glass tubing directly into cup *M* while the three-way stopcock was closed at *O*. When there was sufficient mercury in cup *M* the stopcock was turned so that some mercury flowed out at *P*, then by making communication to the capillary by means of the stopcock a fresh surface of mercury could be caused to enter the capillary *Q*. Before the mercury was allowed to flow into the capillary, the second liquid was put into cup *N* and by turning the stopcock the first portion of the liquid (organic liquid or water) was allowed to flow out at *P*. The stopcock was then turned so that the mercury would rise slowly into the capillary. Since the capillary had already been wetted by organic liquid, or water, it was believed that a stable film had been formed on the wall and that the interfacial contact angle formed between the mercury and this film would be a zero angle. The values obtained with this apparatus are given in Table II.

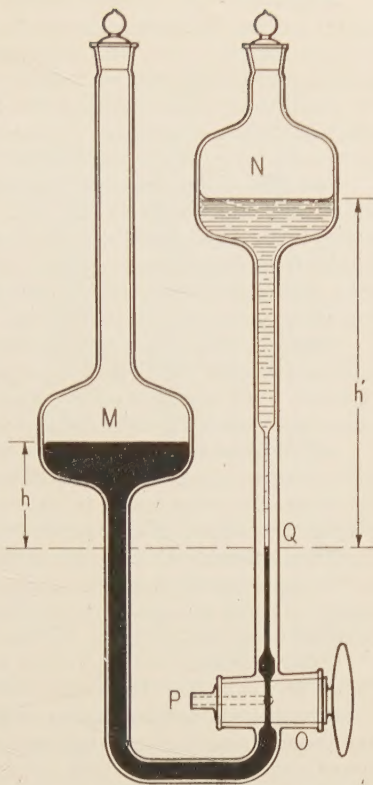


Fig. 2—Capillary rise method for interfacial tensions of mercury against liquids.

Purification of Liquids

The liquids used were liquids for which the physical constants had already been accurately determined and the method of preparation in a pure state carefully studied.⁵

Alcohols.—The alcohols used were refined alcohols and were further treated by distillation from a small amount of potassium hydroxide and silver nitrate to remove traces of aldehydes. They were then dehydrated with quicklime and distilled from the lime, and finally made anhydrous by the use of metallic magnesium and iodine according to the method of Lund and Bjerrum.⁶

(4) Cf. Bartell and Miller, *J. Am. Chem. Soc.*, **50**, 1961 (1928).

(5) Timmermans and Martin, *J. chim. phys.*, **23**, 733 (1926); **25**, 411 (1928).

(6) Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

***n*-Hexane.**—The synthetic hexane of Eastman Kodak Company was used. It was further purified by washing repeatedly with concentrated sulfuric acid, then with alkaline permanganate, then with water, was refluxed with mercury, then dried with fused potassium hydroxide, then with sodium and finally distilled twice from fresh sodium.

***n*-Heptane.**—The *n*-heptane was obtained from the Research Laboratories of the Ethyl Gasoline Corporation. It was of high purity and received no further chemical purification except that it was distilled from sodium before use.

Benzene.—Thiophene-free benzene was stirred for three days with concentrated sulfuric acid using fresh acid each day. It was then washed twice with water, then with sodium hydroxide solution, next dried with fused calcium chloride and then fractionally distilled from phosphorus pentoxide. Finally it was fractionally crystallized eight times when the crystals were perfectly transparent and of a very large size. It was distilled from phosphorus pentoxide before use.

Toluene.—This was synthesized from *p*-bromotoluene by means of the Grignard reaction and then the Grignard compound was hydrolyzed with hydrochloric acid in ice water. The toluene layer was separated, dried with calcium chloride, refluxed with sodium and then fractionally distilled three times from sodium.

***n*-Propylbenzene and *n*-Butylbenzene.**—The *n*-propylbenzene and *n*-butylbenzene were synthetic products previously prepared in this Laboratory.⁷ Owing to their high purity they were merely refluxed with sodium before distillation from fresh sodium to ensure the removal of any traces of halogen compounds.

Nitrobenzene.—A C. P. grade of nitrobenzene was washed with dilute hydrochloric acid to remove basic impurities, and it was then allowed to stand over potassium carbonate. It was next steam distilled and dried over potassium carbonate. Finally it was fractionally distilled twice, and fractionally crystallized twice.

Water.—Ordinary distilled water was distilled from alkaline permanganate through a block tin condenser. It was then redistilled from quartz.

Mercury.—Redistilled mercury was repeatedly shaken with dilute nitric acid to a gray mercury emulsion and then washed thoroughly with water; next it was dried and filtered through a hard filter with a pin point opening. It was then redistilled twice in a current of air at low pressures according to the method of Hulett.⁸

The densities and boiling points of all liquids checked closely with the critical values given by Timmermans and Martin. The freezing point was taken only for benzene and was $5.51 \pm 0.02^\circ$, which checks with the best values for this constant.

Results and Discussion

In Table I are given the interfacial tension values obtained by the drop weight method for mercury in contact with each of twelve pure liquids which are without chemical action on the mercury. For water, nitrobenzene and hexane against mercury, the results show close agreement with accepted values. In the other cases in which values were available for comparison the deviations ranged from 4 to 13 dynes per cm.⁹

A study of the interfacial tension values with mercury is interesting because, unlike most liquid-liquid systems, the mutual solubility is negligibly small. This absence of solubility makes possible the accurate calculation of the work of adhesion between mercury and other liquids without involving solubility effects.

(7) They were prepared by G. L. Mack by means of the Wurtz-Fittig reaction and also purified by him. Acknowledgment is gratefully made to him for the use of these liquids.

(8) Hulett, *Phys. Rev.*, **33**, 307 (1911).

(9) Harkins, "International Critical Tables," Vol. IV, p. 438.

TABLE I

INTERFACIAL TENSION OF MERCURY AGAINST VARIOUS LIQUIDS AT 25° BY THE DROP WEIGHT METHOD

Liquid	Density	(M) Uncorrected drop weight, g.	(m) g.	$f\left(\frac{r}{v^{1/3}}\right)$	Interfacial tension dynes/cm., calcd.	From literature ^a (20°)
Water	0.9970	0.1163	0.0086	0.7240	374.1	375
Ethyl alcohol	.7850	.1151	.0067	.7235	376.9	364
<i>n</i> -Propyl alcohol	.7993	.1152	.0068	.7235	376.5	368
<i>n</i> -Butyl alcohol	.8058	.1141	.0068	.7231	372.8	...
Isoamyl alcohol	.8125	.1145	.0069	.7232	373.7	261.3
Hexane	.6570	.1150	.0056	.7235	379.9	378
Heptane	.6794	.1147	.0058	.7233	378.7	...
Benzene	.8736	.1119	.0072	.7222	364.3	351.2
Toluene	.8622	.1113	.0070	.7218	363.6	359
<i>n</i> -Propylbenzene	.8574	.1113	.0070	.7218	363.1	...
<i>n</i> -Butylbenzene	.8561	.1111	.0070	.7217	362.5	...
Nitrobenzene	1.1980	.1100	.0097	.7212	349.5	350.5

^a "International Critical Tables," Vol. IV, p. 438.

On the basis of the data now available, a comparison of the interfacial tension relationships can be made between liquid-liquid systems in which the mutual solubility is appreciable and those in which it is negligible.

First, in the case of slightly miscible systems as those of most organic liquids with water, it is well known that if in an homologous series of such organic liquids against water, the mutual solubility decreases as the series is ascended, the interfacial tension between the co-existing phases will be found to increase in this series. Thus in this case the interfacial tension and the surface tension of the organic liquid vary in the same direction in the series.

Second, in the case of systems in which the mutual solubility is so small as to be considered negligible, very little difference in interfacial tension values in the homologous series is noted. Examples of such behavior are furnished by the systems mercury with organic liquids, and water with the

TABLE II

INTERFACIAL TENSION OF MERCURY AGAINST VARIOUS LIQUIDS AT 25° BY THE CAPILLARY RISE METHOD

$$d_{\text{Hg}} = 13.534 \text{ g./cc.} \quad r = 0.03201 \text{ cm.}$$

Liquid	Density	h' , cm.	h	Meniscus correction $1/8r(d - d')$	Interfacial tension, dynes/cm.
Hexane	0.6570	14.070	2.455	0.137	378
Benzene	.8736	14.170	2.600	.135	361
Water	.9970	15.070	2.870	.133	375
Nitrobenzene	1.1980	14.350	2.910	.131	350

 r = radius of capillary d = density of mercury d' = density of lighter liquid h = height of lighter liquid surface above meniscus h' = height of mercury surface above meniscus (see Fig. 2)

paraffin hydrocarbons such as hexane and octane (see Tables III and IV). It is believed worth while, however, to point out that the values in the tables do show a slight regular difference in each homologous series against mercury and also for the paraffin hydrocarbons against water, and, if this difference is real, it must be due to effects other than those attributable to

TABLE III

INTERFACIAL TENSION VALUES OF DIFFERENT MEMBERS OF AN HOMOLOGOUS SERIES OF ORGANIC LIQUIDS AGAINST MERCURY, OBTAINED WITH DROP WEIGHT METHOD

Liquid	Interfacial tension against mercury at 25°	Liquid	Interfacial tension against mercury at 25°
Ethyl alcohol	376.9	Benzene	364.3
<i>n</i> -Propyl alcohol	376.5	Toluene	363.6
<i>n</i> -Butyl alcohol	372.8	<i>n</i> -Propylbenzene	363.1
Isoamyl alcohol	373.7	<i>n</i> -Butylbenzene	362.5

TABLE IV

INTERFACIAL TENSION VALUES OF DIFFERENT MEMBERS OF AN HOMOLOGOUS SERIES OF ORGANIC LIQUIDS AGAINST MERCURY AND AGAINST WATER, OBTAINED WITH DROP WEIGHT METHOD

Liquid	Interfacial tension against mercury at 25°	Interfacial tension against water at 20°
<i>n</i> -Hexane	379.9	51.1 ± 0.2
<i>n</i> -Heptane	378.7	
<i>n</i> -Octane	376.0	50.81 ± 0.1

mutual solubility. Further, the order of decreasing interfacial tension values is, in every case, the same as the order of increasing surface tension values of the organic liquids in the homologous series. Considering the interfacial tension values to be dependent upon the difference between the surface tensions of the two phases in equilibrium with each other, we may conclude that *in absence of solubility*, the interfacial tension values for the members of an homologous series against a given liquid will decrease progressively if the surface tension values of the organic liquids increase progressively in the series. It will be noted that this relationship is just opposite to the one which obtains for systems in which the mutual solubility is appreciable.

The Interfacial Tension of Mercury in Contact with Organic Halogen Compounds.—In addition to the data given in the preceding tables, interfacial tension measurements were made with the liquids chlorobenzene bromobenzene, ethylene chloride and ethylene bromide. Although these measurements were carefully made, the results are not included in Table II in the belief that they may not be as reliable as those recorded, due to the impossibility of avoiding chemical reaction of these liquids with mercury.

That these liquids as ordinarily prepared and used tend to give erroneous values is clearly shown by our measurements with ethylene bromide. For the interfacial tension of mercury against a sample of ethylene bromide

which had been purified by the usual chemical methods and then distilled a value was obtained which was in agreement with that obtained by Harkins and Grafton for this system. The ethylene bromide was then subjected to further purification. It was agitated with mercury for six hours (the mercury surface remained bright), ten times fractionally crystallized, and finally distilled under nitrogen at low pressures (to minimize any danger of the liberation of free bromine by displacement by oxygen of the air). When the interfacial tension was measured with this new sample, a value of 346 dynes/cm. at 25° was obtained—20 dynes higher than the previous value.

It is seen that deductions made from interfacial tension measurements of mercury against even the most carefully purified halogen or sulfur compound may be untrustworthy. The value may not represent the true free surface energy value between mercury and the compound, but instead may represent the free surface energy relation between mercury and a very dilute solution consisting of capillary active impurities and the otherwise pure liquid. This would apply in the case of organic compounds of iodine and sulfur and probably to most organic compounds of bromine, especially aliphatic bromides. The instability or reactivity (with oxygen and moisture as well as with metals themselves) of organic halogen compounds (especially saturated aliphatic bromides and iodides) and sulfides is common knowledge, and therefore the danger of formation of capillary active impurities (mercury salts of the halogens or sulfur) is always present. We have obtained values for some carefully purified organic halogen compounds which we believe are not far from the true values; for chlorobenzene, the interfacial tension obtained against mercury was 353 dynes per cm., for bromobenzene 347 and for ethylene chloride 358, all at 25°. The work with organic compounds of halogens would indicate that the specific effects (*i. e.*, attraction of the halogen radicals toward the mercury atoms) are not as strong as has previously been believed.¹⁰

Summary

1. Measurement of interfacial tension of pure liquids against mercury with both the drop weight method and the capillary rise method gave results showing close agreement, indicating that either the dynamic method or the static method is suitable for such measurements. Some of the results obtained did not show close agreement with generally accepted values in the literature.

2. Interfacial tension values were obtained for certain halogen derivatives against mercury. These values are higher than those previously recorded.

3. Interfacial tension values were obtained for some liquids against mercury for which no data are given in the literature.

(10) Harkins and Grafton, *J. Am. Chem. Soc.*, **42**, 2534 (1920); Harkins and Ewing, *ibid.*, **42**, 2539 (1920).

4. Data obtained for an homologous series of organic liquids against mercury indicated that, in the absence of solubility effects, the interfacial tension values of the members of an homologous series against a given liquid will decrease progressively if the surface tension values of the organic liquids increase progressively in the series.

THE SURFACE TENSION OF MERCURY AND OF WATER IN CONTACT WITH SATURATED VAPORS OF ORGANIC LIQUIDS

Introduction

It was predicted by Gibbs¹ that if the surface tension of mercury were measured in contact with a saturated vapor of another liquid, as with water vapor, the value of this surface tension would be equal to the interfacial tension of mercury against liquid water (σ_{12}) plus the surface tension of liquid water in contact with its own vapor (σ_{23}). If σ_{13} be taken to represent the value of the surface tension of mercury against the saturated vapor of the other liquid, then

$$\sigma_{13} = \sigma_{12} + \sigma_{23} \quad (1)$$

This relation obtains because a film of liquid is adsorbed or is condensed on the mercury from the saturated vapor. Gibbs believed that at saturation vapor pressures the condensed film would be of such thickness that its interior would have the properties of a phase in mass.

The thermodynamic condition that governs the application of equation (1) is that the surface tension of the mercury in the presence of its own vapor, σ_1 ,² must be greater than the sum of σ_{12} and σ_{23} .

Previous Results for Films on Mercury.—The experimental data previously used by Iredale³ to test equation (1) for mercury surfaces indicate that this equation holds for saturated water vapor in contact with mercury but not for other saturated vapors against mercury. The measured surface tension value of mercury in the presence of the saturated vapor was in every case (except for water) greater than the sum of the interfacial

(1) Gibbs, "Collected Works of J. Willard Gibbs," Longmans, Green and Co., New York, 1928, Vol. I, p. 235, *cf.* p. 258.

(2) In the designation of surface and interfacial tensions, the use of the symbol σ with two numbers for a subscript represents the surface or interfacial tension between two phases mutually saturated with each other and in equilibrium in contact with each other. In case only one number appears as a subscript, the symbol then stands for the surface tension of a pure liquid in contact with its own vapor and air.

(3) Iredale, *Phil. Mag.*, [6] **49**, 603 (1925).

tension value of mercury against the other liquid, and the surface tension value of the liquid, *i. e.*, $\sigma_{13} > \sigma_{12} + \sigma_{23}$. For benzene the measured value, σ_{13} , was greater by 3.1%, for methyl acetate 4.3%, for ethyl alcohol 7.5%, and for methyl iodide 3.0%. These deviations were considered to be greater than could be accounted for by experimental error.

Iredale³ attempted to explain these results on the basis that Gibbs deduced his relation on the assumption that the films formed on the surface from the saturated vapors were sufficiently thick to have the properties of a phase in mass, whereas the films actually formed were probably monomolecular in thickness and that it did not follow that the tension of such films would be the same as that of liquid in mass (*i. e.*, σ_{13} would not necessarily equal $\sigma_{12} + \sigma_{23}$).

The fact that for all but the water system, $\sigma_{13} > \sigma_{12} + \sigma_{23}$ indicates that from the thermodynamic standpoint equilibrium was attained with the water films and not with films of other liquids.

In searching for causes for the discrepancies, it seemed to us possible that traces of capillary active impurities might have been present in the various liquids used. This would be especially serious in the determination of σ_{12} values since very minute traces of an impurity capable of reacting with the mercury surface can cause an appreciable lowering of the interfacial tension. The fact that water can be more readily obtained in a pure state than can the other liquids mentioned, seemed significant. Another possible source of error might lie in the effect of temperature variations. It is true that so far as the measurements of σ_{12} are concerned, variations of even two or three degrees would be of little effect owing to the small temperature coefficient (about 0.2 dyne per degree)⁴. But in the measurement of σ_{13} isothermal conditions are obviously necessary in order that no evaporation or condensation with respect to the film shall be brought about by temperature differences in the system.

It seemed advisable to carry out new measurements of σ_{12} and σ_{13} using liquids that could be obtained in a very pure state and which were known to be without chemical action on the mercury. The method which was selected as the most reliable for the measurements with mercury was the drop weight method as developed by Harkins and co-workers and as used with mercury by Harkins, Grafton and Ewing,⁵ by Iredale⁶ and by Micheli.⁷

Experimental Work with Films on Mercury

The measurements of the surface tension of mercury in the presence of the saturated vapors (σ_{13}) were carried out at the same time as the interfacial tension measurements for mercury in contact with the liquids (σ_{12}). In both cases the drop weight method was employed.

(4) Harkins and Ewing, *J. Am. Chem. Soc.*, **42**, 2539 (1920).

(5) Harkins and Grafton, *ibid.*, **42**, 2534 (1920); Harkins and Ewing, *ibid.*, **42**, 2539 (1920).

(6) Iredale, *Phil. Mag.*, [6] **45**, 1088 (1923); **48**, 177 (1924).

(7) Micheli, *ibid.*, [7] **3**, 895 (1927).

The *interfacial* tension measurements have already been described in a previous paper.⁸ The measurements of the *surface* tension of the mercury in the presence of the saturated vapors of the organic liquids were carried out in the following manner. Two or three drops of the pure organic liquid were distilled directly into two of the drop weight apparatus cups which were then covered with ground-glass plates and allowed to stand for about one hour in the thermostat before measurements were started. The drop weight apparatus was provided with a small bulb⁹ in which a few drops of the liquid could be placed to aid in saturating the vapor space.

In making the measurements of σ_{13} it is very important to place the drop weight apparatus cup in position with a clamp (a test-tube clamp is convenient) because the heat of the hand would cause vaporization of liquid with subsequent supersaturation and condensation on the cooler portions of the apparatus, *i. e.*, on the tip and the drop. This, of course, would cause erratic results and would completely invalidate the measurement. Even if the hand is touched for a moment to the cup a blur appears on the tip showing condensation due to distillation.

Seven or eight drops were usually collected in each cup. The drops were allowed to form in the course of about three minutes and then by lowering the head of mercury by means of a ratchet and pinion they were allowed to detach in the course of about two minutes.

In the measurements of σ_{13} , the surface tension of mercury against saturated vapors, it was found that while the organic vapors condensed very readily on the mercury to give the tension equal to $\sigma_{12} + \sigma_{23}$, in the case of water vapor it was necessary to allow the drops of mercury to form very close to the water surface in the cup, and to allow about five minutes for the detachment of the drop after it had formed. By operating in this manner reproducible results were obtained and the measurements of σ_{13} for water gave the value equal to $\sigma_{12} + \sigma_{23}$. Iredale had already made the observation that water vapor did not readily condense on mercury surfaces. Very recently Cassel and Salditt¹⁰ found that the surface tension of mercury when measured in the presence of different partial pressures of water vapor in the absence of air at 50° remained unaffected (*i. e.*, the same as *in vacuo*), even when the water vapor pressure was 62 mm.

The method of purification of the liquids used has been given in the preceding paper.

Discussion of Results for Films on Mercury

In Table I (A) are given the measurements made of σ_{13} , and also in the same table are summarized the data to test equation (1).

From a comparison of column 3 with column 6 of the table it will be seen that the relation $\sigma_{13} = \sigma_{12} + \sigma_{23}$ holds within 0.5% and less (the average deviation is about 0.3%) which is within the experimental error for all the films measured. This indicates that all the films formed were in true equilibrium and that equation (1) holds when correct data are used.

It will be observed that equation (1) represents in fact Antonoff's rule¹¹ which is usually stated in the following form: the interfacial tension between two liquids mutually saturated with each other is equal or approximately equal to the difference between the surface tensions of the two phases, each in contact with the vapor of the other phase.¹² This rule

(8) *J. Am. Chem. Soc.*, **55**, 2419 (1933).

(9) For a sketch of the apparatus see Ref. 8.

(10) See Cassel and Salditt, *Z. physik. Chem.*, **A155**, 321 (1931).

(11) Antonoff, *J. Chim. phys.*, **5**, 372 (1907).

(12) It has been stated by Harkins (Alexander, "Colloid Chemistry," The Chemical Catalog Co.,

TABLE I

THE SURFACE TENSION OF MERCURY IN THE PRESENCE OF SATURATED VAPORS IN AIR AT 25°, TABLE (A)

To test the equation, $\sigma_{13} = \sigma_{12} + \sigma_{23}$, for films on mercury compare col. 3 with col. 6

	(A)			(B)		
	(1)	(2)	(3)	(4) ^a	(5) ^b	(6)
	Uncorr. drop weight, g.	$f \{r/1^{1/2}\}$	Surface tension (Hg-vapor) σ_{13} (dynes/ cm.)	Interfacial tension (Hg-liquid) σ_{12} (dynes/ cm.)	Surface tension of liquid σ_{23} (dynes/ cm.)	$\sigma_{12} + \sigma_{23}$ = (4) + (5)
Water	0.1299	0.7294	447.6	374.0	72.0	446.0
Ethyl alcohol	.1156	.7238	401.3	376.6	22.0	398.6
<i>n</i> -Propyl alcohol	.1149	.7235	399.1	376.5	23.3	399.8
<i>n</i> -Butyl alcohol	.1142	.7231	397.1	373.1	24.2	397.3
Isoamyl alcohol	.1142	.7231	397.1	374.0	23.9	397.9
Hexane	.1154	.7236	398.4	380.1	18.0	398.1
Heptane	.1151	.7235	399.8	378.5	19.8	398.3
Benzene	.1131	.7226	393.3	364.4	28.2	392.7
Toluene	.1123	.7222	390.8	362.9	28.0	390.9
<i>n</i> -Propylbenzene	.1129	.7226	392.7	363.0	28.5	391.5
<i>n</i> -Butylbenzene	.1129	.7226	392.7	362.4	28.7	391.1
Nitrobenzene	.1133	.7228	393.7	349.4	42.8	392.2

^a Bartell, Case and Brown, *J. Am. Chem. Soc.*, **55**, 2419 (1933).

^b The surface tensions of the organic liquids σ_{23} were taken from Hennaut-Roland and Lek (International Bureau of Physical Chemical Standards), *Bull. soc. chim. Belg.*, **40**, 177 (1931); *Chem. Abstracts*, **25**, 5322 (1931), and from the "International Critical Tables," Vol. IV.

was based on results of a limited experimental study. Reynolds¹³ in a series of measurements by the capillary rise method found that the rule held closely. Examination of the systems used by him shows that for these cases σ_1 was greater than $\sigma_{12} + \sigma_{23}$. For one system, however, carbon bisulfide and water, he made the observation that the rule did not apply, and he attributed this to impurities in the carbon bisulfide. As a matter of fact, the rule should not apply to the system carbon bisulfide and water because for this system $\sigma_1 < \sigma_{12} + \sigma_{23}$ and as Hardy¹⁴ had already pointed out for such systems, no continuous *liquid* film of the organic liquid can form on the surface of the water.

In a recent paper Antonoff¹⁵ reiterates that his rule is of universal application, and that the reason other investigators (Hardy, Harkins) obtained exceptions to his rule was because of their failure to obtain equilib-

New York, 1926, Vol. I, p. 216) that Antonoff's rule does not apply to the calculation of the interfacial tensions of mercury in contact with other liquids. It was shown above that equation (1) (which embodies Antonoff's rule) does hold for mercury in contact with other liquids. It appears that in the cases which have been cited as indicating failure of Antonoff's rule when applied to mercury, the surface tension of mercury saturated with an organic liquid or with water was, apparently by mistake, assumed to be the same as that of mercury in a vacuum or in an inactive gas at ordinary pressures, probably because of the extremely low solubility of the liquids in mercury.

(13) Reynolds, *J. Chem. Soc.*, **119**, 466 (1921).

(14) Hardy, *Proc. Roy. Soc. (London)*, **A86**, 610 (1912); **88**, 313 (1913).

(15) Antonoff, *Kolloid-Z.*, **59**, 7 (1932).

rium conditions in the measurements of σ_{13} and σ_{23} . We believe, however, that the work of Hardy and the later experimental work of Harkins (with water against carbon bisulfide and against methylene iodide) has definitely shown that Antonoff's rule is not of general applicability in that it does not hold for cases in which $\sigma_1 < \sigma_{12} + \sigma_{23}$.

Discussion of Results for Films on Water

For films on water surfaces in equilibrium with their supporting phase and the saturated vapor phase the measurements made by Harkins and co-workers¹⁶ are generally held to be the most accurate. Their measurements were made by the drop weight method.

The result they obtained for the systems benzene, isoamyl alcohol and *n*-heptyl alcohol with water are striking,¹⁷ in view of the fact that for these systems the measured value of σ_{13} was found to be less than the sum of $\sigma_{12} + \sigma_{23}$. In these systems $\sigma_1 > \sigma_{12} + \sigma_{23}$ and yet these results would indicate that equation (1) does not hold. However, the difference between the values of σ_{13} and $\sigma_{12} + \sigma_{23}$ in these cases seems greater than one might reasonably expect. In the case of *n*-heptyl alcohol, for example, the value of the surface tension of the dry liquid at 20° is given by Harkins as 26.97, whereas the International Bureau of Physical Chemical Standards¹⁸ gives 24.42 dynes/cm. For the interfacial tension of benzene against water Harkins and Humphrey¹⁹ have obtained lower results with the capillary rise method than with the drop volume, but Harkins has accepted the value given by the drop volume method.

In view of these facts it was decided to make measurements for a few systems of organic liquids with water. The capillary rise method was used for both the surface tension and interfacial tension measurements. When these measurements were made it was found that equation (1) held closely for all the cases studied, including benzene with water, for which system measurements were carried out at both 20 and 25°. The results are given in Table II.

The surface tension measurements were carried out in an apparatus of the Richards²⁰ type. It is an absolutely essential precaution, necessary in making measurements with this apparatus of the surface tension of water saturated with an organic liquid, *i. e.*, in equilibrium with the saturated vapor, that the ground glass joint above the capillary tube be kept moist with the organic liquid to ensure the saturation of the vapor space with respect to the organic liquid. Otherwise a mercury seal at this joint

(16) Harkins, "Colloid Symposium Monograph," 1928, Vol. VI, p. 23.

(17) We need not consider the systems carbon bisulfide and methylene iodide with water because for these systems $\sigma_1 < \sigma_{12} + \sigma_{23}$ and no stable film registering the tension $\sigma_{12} + \sigma_{23}$ could form, *i. e.*, equation (1) does not apply.

(18) Hennaut-Roland and Lek, *Bull. soc. chim. Belg.*, **40**, 177 (1931); *Chem. Abstracts*, **25**, 5322 (1931).

(19) Harkins and Humphrey, *J. Am. Chem. Soc.*, **38**, 236, 242 (1916).

(20) Richards and Coombs, *ibid.*, **37**, 1656 (1915).

TABLE II

SUMMARY OF THE VALUES OBTAINED BY THE CAPILLARY RISE METHOD FOR THE INTERFACIAL TENSION OF WATER AGAINST ORGANIC LIQUIDS (σ_{12}), AND THE SURFACE TENSION AGAINST THE SATURATED VAPORS (σ_{13})

Liquid	(1) Temp., °C.	(2) Inter- facial tension of water against org. liq., σ_{12}	(3) Surface ^a tension of org. liq., σ_{23}	(4) $\sigma_{12} + \sigma_{23}$ = (2) + (3)	(5) Surface tension of water satd. with org. liq. obs., σ_{13}
Benzene	20	34.21	28.82	63.03	63.01
Benzene	25	33.91	28.23	62.14	62.12
Toluene	25	35.68	27.97	63.65	63.70
<i>n</i> -Propylbenzene	25	39.08	28.52	67.60	67.98
<i>n</i> -Butylbenzene	25	40.64	28.72	69.36	69.09
Nitrobenzene	25	25.15	42.76	67.91	67.70
Carbon tetrachloride	25	43.50	26.15	69.65	69.66

^a The surface tension of the dry organic liquid and the surface tension of the organic liquid when saturated with water were not appreciably different for the above organic liquids.

must be used, and a small receptacle with some of the organic liquid must be kept in the vapor phase above the capillary tube.

The radius of the capillary was calculated over the part of the tube used, by measurements of the rise of conductivity water and also of pure benzene, accepting 72.79 at 20° and 72.08 at 25° as the surface tension of pure water, and 28.23 as the surface tension of pure benzene at 25°. The value of the radius over the part of the capillary that was used was 0.019465 cm. with water and 0.01946 cm. with benzene. The capillary tube was one selected for its uniformity of bore.

The interfacial tension values were measured with the Bartell-Miller²¹ capillary rise apparatus. It is in general more difficult to apply the capillary rise method to the measurement of interfacial tensions (liquid-liquid) than to the measurement of surface tensions (liquid-vapor) because contact angles at the solid-liquid-liquid interface are more prevalent than at the solid-liquid-vapor interface.

However, it is believed that for the systems studied in this work (Table II) the interfacial contact angle was approximately zero. In the first place, the water had a markedly higher adhesion for the walls of the capillary than did the organic liquids. (A soft glass capillary was used because water exhibits a higher degree of adhesion for soft glass than for Pyrex.) Furthermore, the capillary was coated with a water film before the organic liquid was allowed to enter. Under these conditions, the water film seemed to be stable in the presence of the organic liquid; in fact, the measurements were limited to the systems listed in Table II for this reason.

The radius of the capillary of the interfacial tension apparatus was de-

(21) Bartell and Miller, *J. Am. Chem. Soc.*, **50**, 1961 (1928).

terminated by the use of mercury threads. The value obtained was 0.03249 cm. It has been the practice in the use of this latter method to obtain the radius of the capillary by calculation from measurements for water against benzene, because of the advantage of obtaining the radius at a fixed point, accepting as a standard the value of 35.00 dynes/cm. at 20° or 34.71 dynes at 25° for the interfacial tension of water against benzene (the values obtained in Harkins' laboratory by the drop volume method). By this method the radius obtained was 0.03324 cm.—*a discrepancy of about 2.3%.*

This discrepancy is not due to impurities in either the water or the benzene, because repeated measurements were made; the water used was fresh conductivity water and the benzene was highly purified (the directions were given in a preceding paper). It must be that either the interfacial tension values for water against benzene stated above are in error, or else an interfacial contact angle of about 12° existed in the system during the measurement. The evidence obtained in working with this system (*i. e.*, constancy of the position of the meniscus in the capillary, and the reproducibility of the measurements) lead us to believe that the discrepancy is not due to an interfacial contact angle, but is due instead to an error in the value stated above for the interfacial tension of water against benzene.

In favor of the lower value for the interfacial tension between water and benzene, *i. e.*, 33.91 at 25° against 34.71 given by Harkins by the drop volume method, it may be mentioned that for the interfacial tension between water and toluene and other organic liquids such as chlorobenzene and nitrobenzene we have obtained values which check fairly closely with Harkins' values by the drop volume method, and at the most the values are only about 0.2 of a dyne lower, whereas with benzene the discrepancy is 0.8 of a dyne (2.3% discrepancy).

The values given in Table II agree closely (when corrected to the same temperature) with the values obtained by Reynolds¹³ for the same systems. The latter also found excellent agreement in the application of equation (1) to the system water and amyl alcohol, whereas Harkins did not. (The amyl alcohol used by Reynolds was probably isoamyl alcohol though he did not designate which of the amyl alcohols he used.) Reynolds' value for the surface tension of dry amyl alcohol (24.4 dynes/cm. at 18° or corr. to 20° = 24.2) agrees closely with that given by the International Bureau of Physical Chemical Standards²² for isoamyl alcohol (24.32 at 20°), which differs from the value given by Harkins (23.73 at 20°).

The results in Tables I and II show that equation (1) applies when the initial condition that $\sigma_1 > \sigma_{12} + \sigma_{23}$ holds. This is evidently because a film is formed on the surface of the liquid of higher surface tension which lowers the tension to the value $\sigma_{12} + \sigma_{23}$ at saturation vapor pressures. Whether this film is the thick film of Gibbs,¹ or the monomolecular film of Rayleigh,

(22) *Loc. cit.*, Table I, Ref. b.

Devaux and Langmuir, is an important question which, on the basis of existing data,²³ cannot be answered definitely as a general case.

Summary

1. Measurements by the drop weight method were made of the surface tension of mercury in contact with saturated vapors of organic liquids. Different values from those existing in the literature were obtained for some of the liquids, and also values were obtained for a number of liquids for which no previous values appear to have been recorded.

2. Measurements by the capillary rise method were made of the interfacial tension of water in contact with organic liquids, and of the surface tension of water saturated with organic liquids and in contact with the saturated vapor.

3. The results show that when a film is spontaneously formed on the surface of a liquid (*e. g.*, mercury or water), the surface tension of the liquid supporting the film registers at saturation vapor pressures a tension, σ_{13} , the value of which is equal to the sum given by the interfacial tension of the liquid against the liquid constituting the film, σ_{12} , plus the surface tension of the film liquid, σ_{23} , that is, $\sigma_{13} = \sigma_{12} + \sigma_{23}$ at saturation vapor pressures when the initial condition (the condition for film formation) $\sigma_1 > \sigma_{12} + \sigma_{23}$ is fulfilled. In other words, the so-called Antonoff's interfacial tension rule holds for these systems, contrary to the results of some previous investigators.

(23) For evidence of multimolecular films *cf.* Cassel [*Trans. Faraday Soc.*, **28**, 177 (1932)] and for monomolecular films *cf.* Rideal, "Introduction to Surface Chemistry," Cambridge University Press, 1930, pp. 61, 83; Adam, "Physics and Chemistry of Surfaces," Oxford University Press, 1930, p. 29.

